Magnetic and spectroscopic investigations on VI2, MnI2, and FeI2

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SUMMARY

In this thesis the magnetic and spectroscopic investigations, which have been carried out on vanadium-, iron-, manganese-, and some of the other 3d transition-metal diiodides, are described.

In chapter 1 some general remarks are made about the dihalides of the first-row transition metals. The preparation of the diiodides of the 3d transition metals is described in chapter 2. The dichlorides, dibromides and diiodides of the first-row transition metals all have a $Cd(OH)_2$, C6 or a $CdCl_2$, C19 crystal structure. Only the chromium dihalides have a somewhat different structure. The unit-cell dimensions, as obtained by powder X-ray diffraction, are given in this chapter. Because the diiodides are more or less hygroscopic these materials had to be handled carefully. The experimental procedures are given in chapter 2.

In the first part of chapter 3 the results of the magnetic investigations on VI_2, MnI_2, FeI_2, CoI_2, and NiI_2 are given. The Néel temperature of VI_2, 15 ^oK, is low compared to the asymptotic Curie temperature of -140^oK. The susceptibility measurements indicate that short-range magnetic order is present up to 70^oK. High-field magnetization measurements, in magnetic fields up to 350 kOe, have been carried out on FeI_2. With the external field parallel to the crystallographic c axis and at temperatures well below T_N, two major changes in the magnetization were found: one at about 45 kOe and the second at 120 kOe. At fields above 120 kOe the magnetic moments are ordered ferromagnetically. The second part of chapter 3 deals with the magnetic properties of $FeCl_2$, $FeBr_2$ and FeI_2. In these compounds a strong single-ion anisotropy is favouring an orientation of the magnetic moments parallel to the c axis. The exchange and magnetic-anisotropy parameters are determined from the susceptibility data. The metamagnetic transition in $FeCl_2$ and $FeBr_2$ can be described quite well with a simple Néel model, but this is not the case for FeI_2. Neutron powder-diffraction investigations show that, below T_N, FeI_2 has the $MnBr_2$-type of magnetic structure. The magnetic structure of VI_2 is more complicated.

In chapter 4 the stability of magnetic structures in a $Cd(OH)_2$ type crystal structure is discussed. The exchange energy of the magnetic ordering is described in terms of five different exchange interactions, two in the metal-ion layer and three interlayer interactions. The models for the magnetic arrangement, which are discussed, all involve rows of parallel spins in either the $[010]$ or the $[1\bar{1}0]$ direction. Stability diagrams are given for the cases that only intralayer exchange is important, and that the anisotropy is either strong or zero. A general expression is

derived for the magnetic dipolar energy of a helical structure in which all spins are parallel to a certain plane.

In chapter 5 the magnetic structures of the iron dihalides and the manganese dihalides are discussed using the models derived in chapter 4. For a magnetic field along the c axis the first transition in FeI_2 will be a transition from the antiferromagnetic $MnBr_2$-type of structure to a spin-flop state, in which the components of the magnetic moments perpendicular to the c axis have a helical or a 120^o magnetic structure. Calculations show that the interlayer exchange via the nearly straight path of two halogen anions must be strong and that also the fourth-order term in the anisotropy will be large. The magnetic exchange interactions in $MnCl_2$, $MnBr_2$ and MnI_2 are very weak. In these compounds the magnetic dipolar energy also becomes an important factor for the stabilization of magnetic structures. The stability of the peculiar helical structure of MnI_2 is discussed in detail.

In chapter 6 some general aspects of low-temperature absorption spectroscopy of crystalline compounds, containing divalent 3d transition-metal ions, are discussed.

The low-temperature spectra ($5 \leqslant T \leqslant 300^oK$) of VI_2, MnI_2 and FeI_2 are reported in chapter 7. The parity-forbidden transitions in VI_2 are made allowed by the vibronic mechanism. The temperature dependence of the oscillator strength of these bands can be described quite well with the equation for such a vibronic mechanism, a hyperbolic cotangent function containing the frequency of odd-parity fundamental modes in VI_2. Below the Néel temperature many narrow lines are observed in the spectrum of VI_2. These lines disappear when the temperature is raised above T_N and the remaining broad band shifts to lower frequency. Part of the structure in the spectra of VI_2 is ascribed to spin-orbit interaction. The fine structure of some of the absorption bands of MnI_2 is due to a vibrational progression of the totally-symmetric fundamental mode in MnI_2. The Racah parameters and the crystal-field splitting have been calculated from the observed band positions for VI_2, MnI_2 and FeI_2. The reduction of the Racah parameters, with respect to the free-ion values, increases upon going from the dichlorides to the diiodides. This effect is presumably due to an increase of the covalency.